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THE INFLUENCE OF FABRICATION CONDITIONS ON THE PHYSICAL PROPERTIES OF PLZT:Nd^{3+} CERAMICS

WPŁYW WARUNKÓW OTRZYMYWANIA NA FIZYCZNE WŁAŚCIWOŚCI CERAMIKI PLZT:Nd^{3+}

The aim of this work was to study the effect of fabrication conditions and neodymium co-doping on the physical properties of $(Pb_{0.98}La_{0.02})(Zr_{0.65}Ti_{0.35})_{0.98}O_3$, known as PLZT:$Nd^{3+}$ ceramics. All ceramic powders of these materials were synthesized by the conventional mixed oxide method, from the high purity raw materials (>99.9%). The bulk ceramic samples were sintered by the pressure less sintering and the hot-uniaxial pressing techniques.

The study gives a detailed account of the relationships between doping and preparing conditions on the dielectric and optical properties of obtained ceramic materials. Optimal conditions of PLZT:Nd^{3+} preparation as well as Nd^{3+} activator concentration were determined in relation to the potential opto-electronic applications.

Keywords: PLZT, ferroelectric ceramics, luminescence, Nd^{3+}co-doping

Celem niniejszej pracy było zbadanie wpływu warunków wytwarzania i zastosowanej domieszki neodymu na właściwości fizyczne ceramiki $(Pb_{0.98}La_{0.02})(Zr_{0.65}Ti_{0.35})_{0.98}O_3$, określanej mianem PLZT:Nd^{3+}. Wszystkie proszki przygotowanych składów syntetyzowano metodą konwencjonalną, z tlenków o wysokiej czystości (>99.9%). Próbki ceramiczne zagęszczano techniką swobodnego spiekania i jednoosiowego prasowania na gorąco. Wykonane badania dały szczegółowy opis zależności między stosowaną domieszką oraz przyjętymi warunkami wytwarzania oraz wpływu na dielektryczne i optyczne właściwości otrzymanych materiałów ceramicznych. Optymalne warunki przygotowania PLZT:Nd^{3+}, jak również zastosowane stężenia aktywatora Nd^{3+} zostały określone w odniesieniu do potencjalnych zastosowań optoelektronicznych.

1. Introduction

Lanthanum modified lead zirconate titanate (PLZT) ceramic, has been known as ferroelectric material with perovskite structure [1,2], presents various structural phases with dielectric and optical properties, depending on its chemical composition [3].

Since last decades, there has been an increasing interest in rare-earth-doped PLZT ceramics, because it can be easily substituted with lanthanide elements for La^{3+} ions [4]. Such co-doping process can occur without any restrictions up to relatively high concentrations of dopants. As a consequence, electro-optic effects of PLZT:RE^{3+} are up to 20 times larger, than in other optical active crystals [5]. For this reason PLZT:RE^{3+} ceramics are promising for use as some electro-optical elements, optical sources and amplifiers, or multifunction compact devices. Recently, neodymium (Nd^{3+}) doped PLZT material has been investigated for its potential application as a ferroelectric and luminescent laser-host active medium.

The goal of this work was to investigate how fabrication conditions, in this case the pressure less sintering and the hot-uniaxial pressing method, as well as the neodymium dopant ratio influences on PLZT:Nd^{3+} powders and ceramics, like its structure, microstructure, luminescent spectra and basic ferroelectric properties.

2. Experimental procedure

For the measurements were chosen the pure $(Pb_{0.92}La_{0.08})(Zr_{0.65}Ti_{0.35})_{0.98}O_3$ compositions and additionally Nd^{3+} ions co-doped of its compositions, with 0-1wt.% respectively. In this paper, the following abbreviations will be used to determine the compositions of 8/65/35 PLZT, 8/65/35 PLZT:Nd^{3+}0.5 and 8/65/35 PLZT:Nd^{3+}1.

The preparation and synthesis process of un-doped and Nd^{3+}co-doped PLZT powders was performed through the solid state reaction, by the by the conventional ceramic method. Stoichiometric amounts of high purity oxides powders (>99.99% Sigma Aldrich) of PbO, La_2O_3, ZrO_2, TiO_2 and respectively Nd_2O_3 were mixed and grinded in a planetary ball-mill (Pulverisette 6) for 16 h, using YTZ balls as grinding media (of 10 mm in diameter) in ethanol solution, for each composition respectively. Dried and mixed powders, were press in pellets and subsequently calcined in air, at T = 1223K, for 3 h to perform the perovskite phase. During

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synthesis process $PbZrO_3$ powder was used as a lead source in the crucible to minimize volatilization of PbO. Calcined material were remilled for 24 h to reduce the particle size, and then cold pressed into pellets (φ = 10 mm, p = 200 MPa). The consolidation of ceramic samples was performed by: (i) one stage sintering (T_s = 1473K/2 h) by the hot uniaxial pressing method (HUP), and (ii) two-stage pressureless sintering (PS) method (T_{sI} = 1373K/5 h, T_{sII} = 1523K/8 h). Figure 1 presented the flow chart of the PLZT:RE^{3+} ceramics preparation.

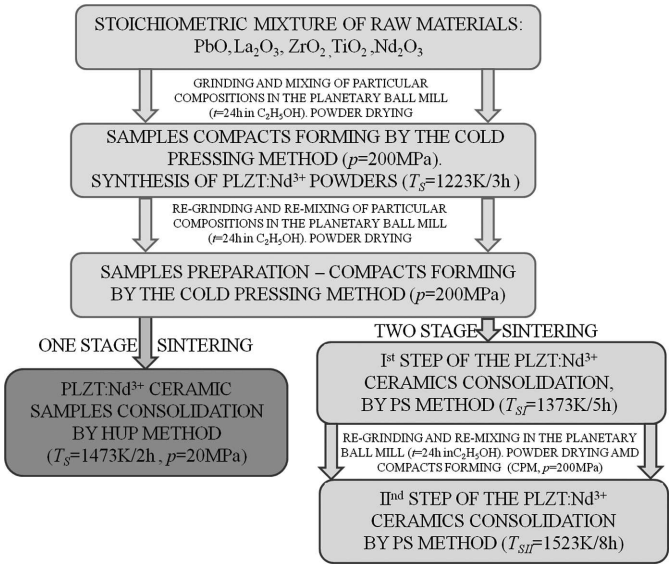

Fig. 1. Scheme of the fabrication process of 8/65/35 PLZT:Nd^{3+} ceramics

The morphologies and grain sizes of synthesized powders were directly imaged using scanning electron microscopy (SEM, HITACHI S-4700). Using the same microscope, with EDS-NORAN Vantage system of microanalysis, was allowed to investigate the stoichiometry of pure and co-doped PLZT:Nd^{3+} synthesized powders.

Formation of the perovskite phase in HUP and PS sintered PLZT:Nd^{3+} ceramics samples were confirmed by X-ray diffraction (XRD; Philips PW 3710), using CuK_α radiation at room temperature. The lattice parameters for PLZT:Nd^{3+} ceramic specimens were calculated using Rietveld refinement, embedded into the computer program PowderCell 2.4.

Reflection spectra were recorded in the region of 250-800 nm on ARC SpectraPro-300i (Acton Research Corporation) spectrometer equipped with 450 W Xenon arc lamp, single photon counting photomultiplier and integration sphere. As reflectance standard barium sulfate was used ($BaSO_4$, 99.998% purity, Alfa Aesar). Excitation and emissions spectra measurements were recorded on Edinburgh Instruments fluorescent spectrometer FSL900 equipped with a 450 W Xenon discharge lamp, in the region of 250-850 nm, and 650-1000 nm, respectively.

Before electrical measurements, all sintered ceramic samples of about 1 cm diameter were cut to give parallel plates of 1 mm thickness, and polished with 1 μm diamond paste to a smooth surface finish. Subsequently the silver paste electrodes were applied to both surfaces of the annealed ceramic samples, and then heated in an oven (T = 423K/1 h) for evaporate of organic solvent from the paste. Impedance meter Quad Tech 1920 working at an excitation frequency of 1 kHz with virtual Sawyer – Tower bridge with digital registration of the date, at frequency 1 Hz were used for dielectric and ferroelectric measurements. Temperature dependence of the real part of dielectric permittivity was measured from T = 300K to T = 650K at a rate of 1K/min., for cooling processes.

3. Results and discussion

The qualitative and quantitative chemical compositions of synthesized PLZT:Nd^{3+} powders were confirmed by the EDS measurements (Fig. 2A). Obtained results are very close to the calculated stoichiometric ratio, in each of prepared composition. It's confirmed also a high purity and homogeneity of semi-agglomerates calcined powders, which revealed the submicron grain sizes ranging (Fig. 2B).

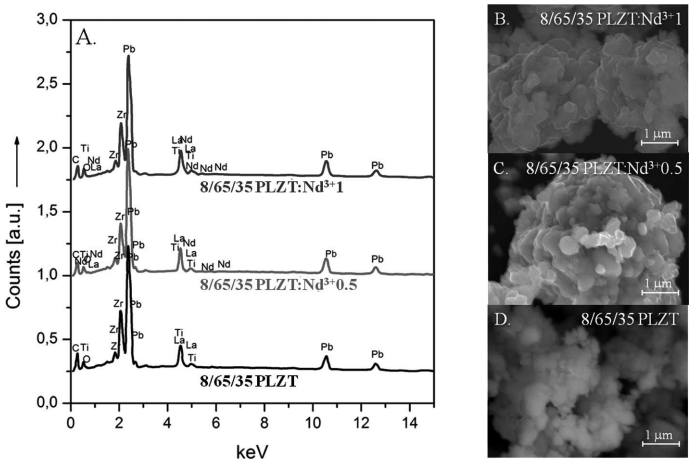

Fig. 2. EDS spectrum and SEM images of PLZT:Nd^{3+} synthesized powders

One can see on the SEM pictures, undoped as well as the neodymium co-doped 8/65/35 PLZT: Nd^{3+} ceramics, were unporous and crystallized in form well shaped grains (Fig. 3). Based on literature [i.e.6], the inhibition of grain growth, was expected as result of neodymium co-doping on 8/65/35 PLZT:Nd^{3+} ceramics. Analysis of the fracture surface (Fig. 3) revealed changes in the morphology of obtained ceramics and their slight growth was observed, regardless of used sintering method. In case of pressureless sintered ceramics, increasing of grains size was observed with higher neodymium content, from r_p ~2 μm for 8/65/35PLZT, to r_p ~4 μm for 8/65/35 PLZT:Nd^{3+}0.5, and up to r_p ~6 μm for 8/65/35 PLZT:Nd^{3+}1. However, the grains growth took place during hot pressing sintering, but such obtained PLZT:Nd^{3+} materials were characterized with smaller grains with size from r_p ~1-1.5 μm for 8/65/35 PLZT, to r_p ~2 μm for 8/65/35 PLZT:Nd^{3+}0.5, and up to r_p ~3 μm for 8/65/35 PLZT:Nd^{3+}1. For this reason probably, from the three of prepared ceramics compositions, only hot pressed 8/65/35 PLZT was transparent, whereas 8/65/35 PLZT:Nd^{3+}0.5 and 8/65/35 PLZT:Nd^{3+}1, were translucent. In case of PS sintering all fabricated samples were opaque for visible light.

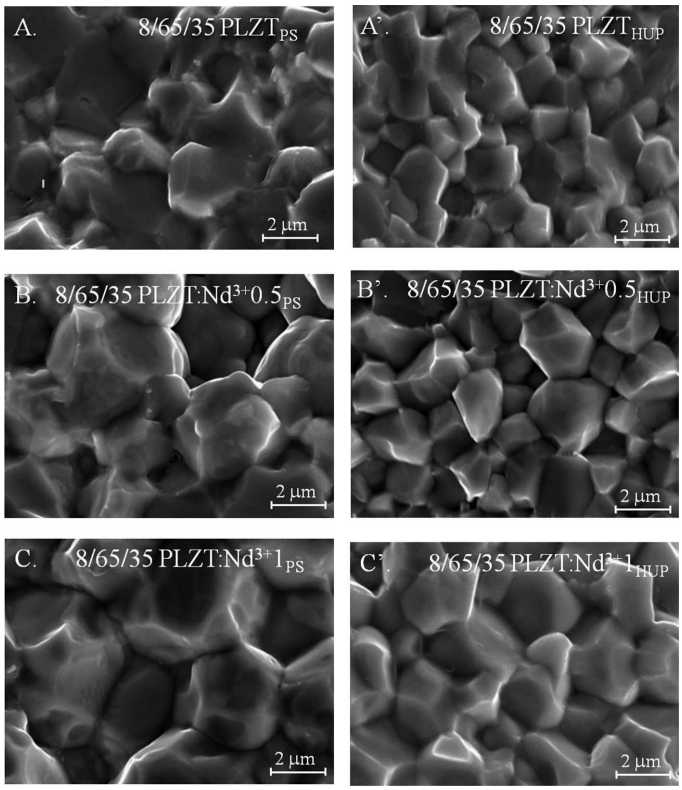

Fig. 3. SEM micrographs of PLZT:Nd^{3+} ceramics, sintered in different conditions PS (A-C) and HUP (A'-C') (mag. 5000x)

All analyzed X-ray diffraction patterns of sintered 8/65/35 PLZT:Nd^{3+} ceramic PS and HUP are shown in Fig. 4. The calculated unit cell parameters, calculated density, volume of the elementary cell and Rietveld analysis parameters size are given in Table 1.

The Rietveld refinement method, fixed into X'Pert High Score (Panalytical, B.V) computer program was used for calculating of the elementary cell parameters. For the diffraction pattern fitting a structure model from ICDD data base was used (PDF standards, N° 00-029-0775; 00-029-0776; 00-046-0336). It was found that each of the PS (two-stages) and HUP (one-stage) sintered PLZT:Nd^{3+} ceramics sample exhibited rhombohedral phase group, *R3m*. One can see, neodymium co-doping (0.5-1wt.%) does not change the symmetry the perovskite lattice structure of 8/65/35 PLZT, regardless of used sintering method. Density of samples was measured by the Archimedes' method and was found to be from 93% to 96% of theoretical density, respectively for PS and HUP obtained PLZT:Nd^{3+} materials.

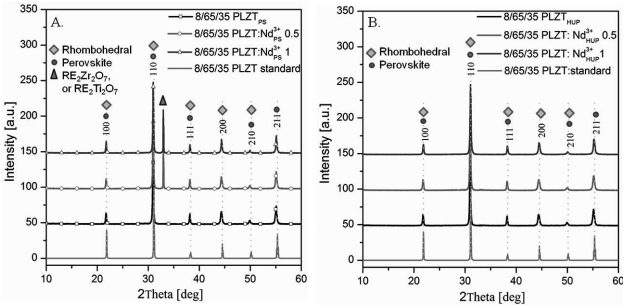

Fig. 4. X-ray diffraction patterns of PS (A) and HUP (B) sintered PLZT:Nd^{3+} ceramics

The low – frequency (1 kHz) temperature dependence on the dielectric constant for 8/65/35 PLZT:Nd^{3+} ceramics is presented in Fig. 5. The neodymium admixture caused shift the temperature of dielectric permittivity maximum (T_m) to low value (Table 2). Moreover the 0.5wt.% of Nd^{3+} dopant significantly increases the maximum value of permittivity. The further increase of it to 1wt.%, leads to reduced of ε_{rmax} (Table 2). The differences are significant for undoped 8/65/35 PLZT, grow up in case of 0.5wt.% of Nd^{3+} and next diminish for higher value of dopant. Additionally the increase of neodymium content leads to broadening of the dielectric permittivity maximum, typical for ferroelectric relaxor materials.

TABLE 1

The lattice parameters of Rietveld fitting, obtained for PLZT:Nd^{3+} ceramics consolidated by PS and HUP methods: diffraction pattern fitting factors: R_p – primary, R_{wp} – weighted, R_{exp} – experimental; a_0[nm], b_0 [nm], c_0 [nm] – parameters of unit cell; V[nm^3] – unit cell volume

PLZT:Nd^{3+} SAMPLES			FITTING FACTORS			SPACE GROUP	CRYSTAL SYSTEM	a_0 [nm]	b_0 [nm]	c_0 [nm]	Vx10^3 [nm^3]
Nd^{3+} wt.%		d [g/cm^3]	R_p	R_{wp}	R_{exp}						
PS	0	7.069	16.90	19.37	11.15	*R3m*	rhombohedral	0.5652	0.5652	0.7376	204.78
	0.5	7.166	16.77	22.03	15.87	*R3m*	rhombohedral	0.5665	0.5665	0.7350	204.85
	1	7.462	17.27	23.92	25.01	*R3m*	rhombohedral	0.5675	0.5675	0.7305	203.46
HUP	0	7.856	15.70	18.00	10.04	*R3m*	rhombohedral	0.5762	0.5762	0.7083	205.08
	0.5	7.845	16.77	23.71	11.02	*R3m*	rhombohedral	0.5761	0.5761	0.7077	204.95
	1	7.801	23.92	40.33	11.72	*R3m*	rhombohedral	0.5759	0.5759	0.7069	204.55

TABLE 2

Ferroelectric parameters obtained for PLZT:Nd^{3+} ceramics sintered by PS and HUP methods (T_0– Curie-Weiss temperature, T_m – Curie temperature, T' – temperature above which applies Curie-Weiss law; ε_{rmax} – permittivity @peak maximum, ε_{rRT} – permittivity @RT, C – Curie-Weiss constant at 1 kHz)

PLZT:Nd^{3+} SAMPLES with Nd^{3+} wt.%		T_0 [K]	T_m [K]	T' [K]	ε_{rmax}	ε_{rRT}	$\varepsilon_{rmax}/\varepsilon_{rRT}$	$C\times 10^5$ [K^{-1}]
PS	0	388	415	506	5996	1711	3.50	4.67
	0.5	335	408	474	6670	2782	2.39	5.01
	1	322	400	482	4601	2217	2.07	6.53
HUP	0	376	420	523	6705	1650	4.06	5.69
	0.5	348	406	506	8628	2782	3.09	5.93
	1	342	398	485	5226	2881	1.81	6.24

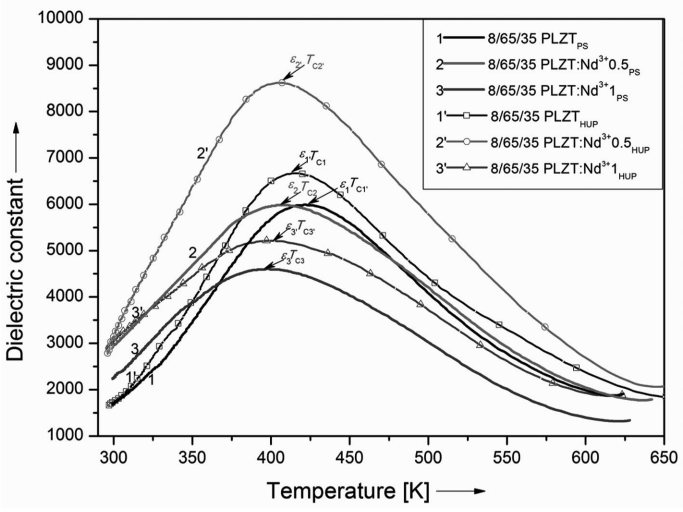

Fig. 5. Dielectric constant as a function of temperature, measured at f = 1 kHz for the 8/65/35 PLZT:Nd^{3+} ceramics (cooling process)

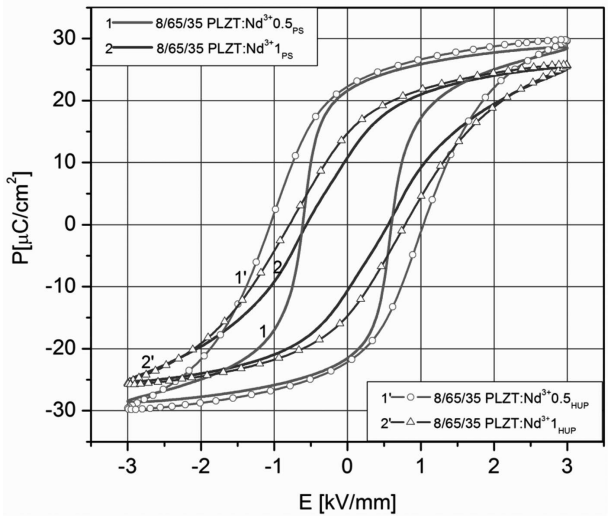

Fig. 6. P-E hysteresis loops of the 8/65/35 PLZT:Nd^{3+} ceramics

Ferroelectric properties of 8/65/35 PLZT:Nd^{3+} materials were proved by measurements of the ferroelectric hysteresis loops. Also in this case, as can be seen at the $P(E)$ dependence graph (Fig. 6), the increase of dopant amount in ceramics composition change the character of the hysteresis loop. The highest ferroelectric properties (spontaneous polarization (P_s) and coercive field (E_c)) were observed for 8/65/35 PLZT:Nd^{3+}0.5 samples, fabricated by HUP method. However, further increasing of the concentration of neodymium ions in 8/65/35 PLZT results in the rapid decrease of P_s and E_c values, as it was recorded for 8/65/35 PLZT:Nd^{3+}1wt.% samples, regardless of used fabrication method. Probably it's effect of higher defect concentrations, which interact with the domain boundaries in obtained materials [7].

An optical property of neodymium ions in several host matrices, such as glasses and ceramics, depends on their chemical composition and conditions of fabrication [8].

Luminescent spectra were measured for all prepared samples, to show the influence of neodymium admixture on 8/65/35 PLZT luminescent properties. Reflection spectra proof, that the reflectivity in the visible range depends on fabricating condition, and is nearly 70% in case of pressureless sintered PLZT:Nd^{3+} ceramics, whereas reaches up to 80% for hot pressed samples, with an absorption process for Nd^{3+} at the $4f^2 \rightarrow 5d$ transitions

The luminescence band located in the near-infrared region can be observed, and it corresponds to $^4F_{3/2}$–$^4I_{9/2}$ (890 nm) transitions of Nd^{3+}. Several bands observed in the reflectance (Fig. 6) and excitation spectra (Fig. 7) correspond to transitions originating from the $^4I_{9/2}$ ground state to the $^2K_{13/2}$, $^4G_{7/2}$, $^4G_{9/2}$ (500-530 nm), $^4G_{5/2}$, $^2G_{7/2}$ (585 nm), $^2H_{11/2}$ (630 nm), $^4F_{9/2}$ (680 nm), $^4F_{7/2}$, $^4S_{3/2}$ (745 nm) and $^4F_{5/2}$, $^2H_{9/2}$ (803 nm) excited states of Nd^{3+}, respectively.

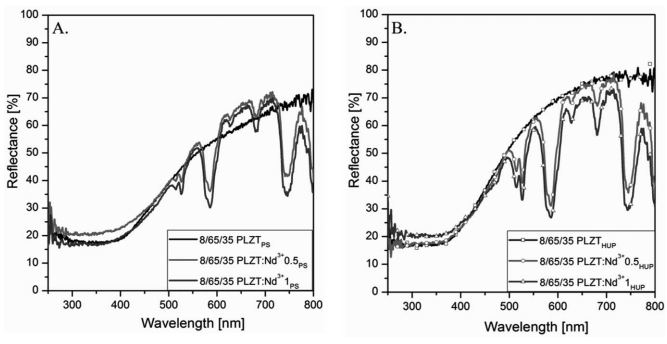

Fig. 7. Reflection spectra of PS (A) and HUP (B) fabricated PLZT:Nd^{3+} ceramics

Near-infrared luminescence band at λ_{em} = 883 nm due to the $^4F_{3/2}-{}^4I_{9/2}$ transition of Nd^{3+} ions was registered under excitation of $^4G_{5/2}$, $^2G_{7/2}$ states by λ_{exc} = 585 nm line (Fig. 8). One can see, the intensity of excitation and emission spectra's depends on fabrication conditions, as well as Nd^{3+} concentration in host lattice of 8/65/35 PLZT. It is approximately twice higher for hot pressed materials, and the highest spectral (excitation and emission) intensities were observed for HUP 8/65/35 PLZT:Nd^{3+}0.5 samples.

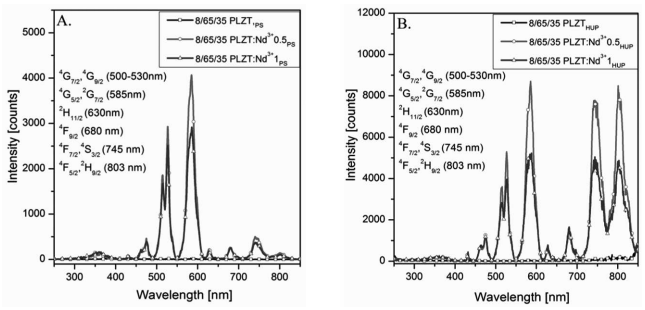

Fig. 8. Excitation spectra of PS (A) and HUP (B) fabricated PLZT:Nd^{3+} ceramics (monitored at λ_{em} = 883 nm)

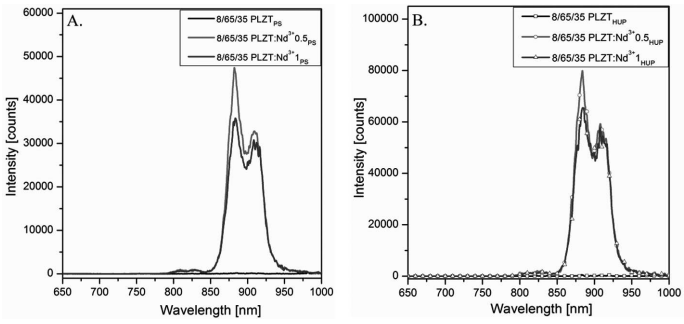

Fig. 9. Emission spectra of PS (A) and HUP (B) fabricated PLZT:Nd^{3+} ceramics (excited at λ_{exc} = 585 nm)

4. Conclusions

Using the conventional ceramics synthesis technique the submicron powders of 8/65/35 PLZT:Nd^{3+}ceramics were prepared. Their structural, microstructural, dielectric, ferroelectric and spectroscopic characterizations were performed, as a function of sintering condition as well as the neodymium dopant. It was found that each of the PS and HUP fabricated 8/65/35 PLZT:Nd^{3+} bulk ceramics samples were exhibited phase perovskite structure, and identified as rhombohedral symmetry, space group *R3m*.

Neodymium co-doped 8/65/35 PLZT, as well as the undoped materials were unporous and crystallized in form well shaped grains. Spectroscopic analysis indicated that PLZT:Nd^{3+} ceramics is a potential active media in the near infrared region, for some photonic applications.

The increase of Nd^{3+} co-dopant reduced the maximum of Curie temperature and displaced it to the low range, made it more diffuse and typical for relaxors type materials. Ferroelectric properties decrease with increase of neodymium co-dopant in 8/65/35 PLZT. Fabrication by HUP method influence on improvement of dielectric and ferroelectric parameters in comparison to the same composition of 8/65/35 PLZT:Nd^{3+} prepared by PS method.

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REFERENCES

[1] R. Sitko, B. Zawisza, J. Jurczyk, D. Bochenek, M. Płońska, Microchim. Acta **144**, 9-15 (2004).
[2] E. Nogas-Ćwikiel, Arch. Mett. Mater. **56**, 4, 1065-1069 (2011).
[3] G.H. Haertling, Piezoelectric and electrooptic ceramics, Ceramic Materials for Electronics, Processing, Properties and Applications, Dekker, New York, 2002.
[4] S. Murakami, M. Morita, M. Herren, T. Sakurai, D. Rau, J. Lumin. **87-89**, 694-696 (2000).
[5] J. Ballato, R. Esmacher, R. Schwartz, M. Dejneka, J. Lumin. **86**, 101-105 (2000).
[6] A.S.S. de Camargo, L.A. de O. Nunes, I.A. Santos, D. Garcia, J.A. Eiras, J. Appl. Phys. **95**, 2135-2140 (2004).
[7] K. Ramam, M. Lopez, J. All. Comp. **466**, 398 (2008).
[8] M. Abril, J. Mendez-Ramos, I.R. Martin, U.R. Rodriguez-Mendoza, V. Lavin, A. Delgado-Torres, V.D. Rodriguez, P. Nunez, A.D. Lozano-Gorrin, J. Appl. Phys. **95**, 5271 (2004).

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